Supporting information

Flexible Film-Type Sensor for Electrochemical Measurement of Dopamine by a Molecular Imprinting Method

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1) Preparation of a DA-PPy electrode on the Surface of a Glassy Carbon Electrode

A glassy carbon electrode (EC Frontier, GC-6355) sufficiently polished with a 0.5% alumina solution was connected to a potentiostat (Toyo Technica, SP -300) as a working electrode, a platinum wire was used as a counter electrode (CE), and a silver/silver chloride electrode was used as a reference electrode (RE). The electrode was immersed in a solution for electropolymerization of PPy (10 mM Pyrrole, 1 mM Dopamine Hydrochloride, 0.1 M SDS in Milli Q, N_2 bubbling for 20 min) in an electrochemical cell installed on a stirrer. The entire system was installed in a shield box covered with aluminum foil to shield external noise.

Electropolymerization of PPy by cyclic voltammetry (Scan speed: 10 mV/s, Scan range: 0 ~ 0.8

V, cycle number: 3 cycles, 100 rpm) provided a mixed layer of polypyrrole (PPy) and dopamine (DA) on the surface of the glassy carbon electrode. The prepared DA-containing PPy film on the glassy carbon electrode was washed with Milli Q and then the CV was swept (Scan speed: 40 mV/s, Scan range: -0.2 – 0.6 V, Cycle number: 60 cycles, 100 rpm) in 0.1 mol/L phosphate buffer solution, which was thoroughly degassed with nitrogen gas (20 min N_2 bubbling) to remove DA from the mixed layer of PPy and DA. Then the surface was washed with Milli Q, and CV (Scan speed: 50 mV/s, Scan range: -0.2 to 1.3 V, cycle number: 30 cycles) was swept again as a working electrode at a wider potential toward the oxidation side than during the elimination of DA in phosphate buffer solution in order to over-oxidize PPy. Thus, a PPy electrode using dopamine (DA) as a molecular template was prepared on a glassy carbon electrode (hereinafter referred to as a DA-PPy carbon electrode). In addition, a system in which DA was not added during PPy electropolymerization was used as a negative control (Hereinafter referred to as PPy electrode).

2) Measurement of Dopamine Using a DA-PPy Carbon Electrode

For the DA-PPy and PPy carbon electrodes, the calibration curves obtained from the current values at 0.24 V are shown in **Figure S1(A)** and **S1(B)**, respectively. The slope averaged for 3 times measurement was 22 ± 3.5 nA/nM for the DA-PPy carbon electrode and 13 ± 3.1 nA/nM for the PPy carbon electrode. It is due to the increase in the amount of DA adsorbed on the DA-PPy carbon electrode, and the effect of molecular imprinting using DA was confirmed.

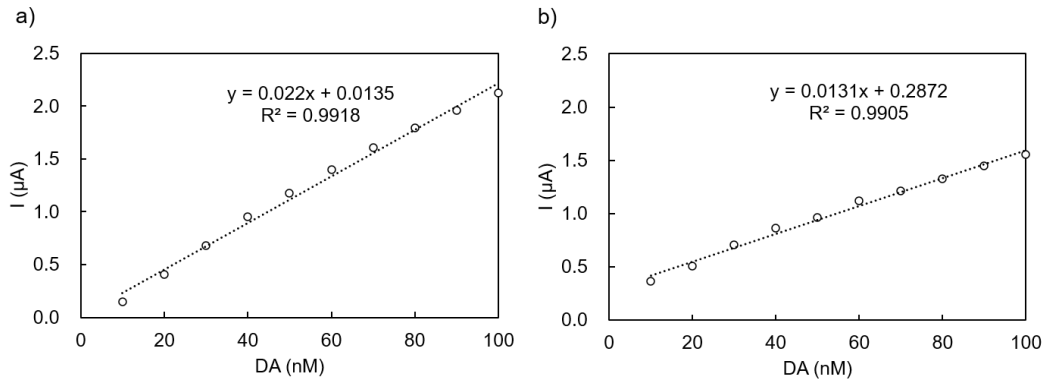

Figure S1 Calibration curves of a) DA-PPy and b) PPy carbon electrodes at the oxidation potential of DA (0.24 V).

3) Selectivity of a DA-PPy Carbon Electrode for the Other Neurotransmitters

In order to evaluate the selectivity of the prepared DA-PPy carbon electrode on the glassy carbon electrode, it was used to measure norepinephrine (NE) and serotonin (5-HT) in a three-electrode system. Concretely, a DA-PPy carbon electrode or a PPy carbon electrode was used as a working electrode and immersed in 0.1 mol/L phosphate buffer, and a 10 μM NE or 5-HT phosphate

buffer was added to this solution to increase the concentrations of NE and 5-HT in 10 nM increments to 100 nM. The oxidation currents of NE or 5-HT were measured by sweeping the SWV with each 10 nM increase.

Different concentrations of neurotransmitters (DA, NE, and 5-HE) were subjected to SWV measurements to determine the oxidation potential of each transmitter. **Fig. S2** shows voltammograms of 100 nM DA, 1000 nM NE and 100 nM 5-HT using a DA-PPy carbon electrode.

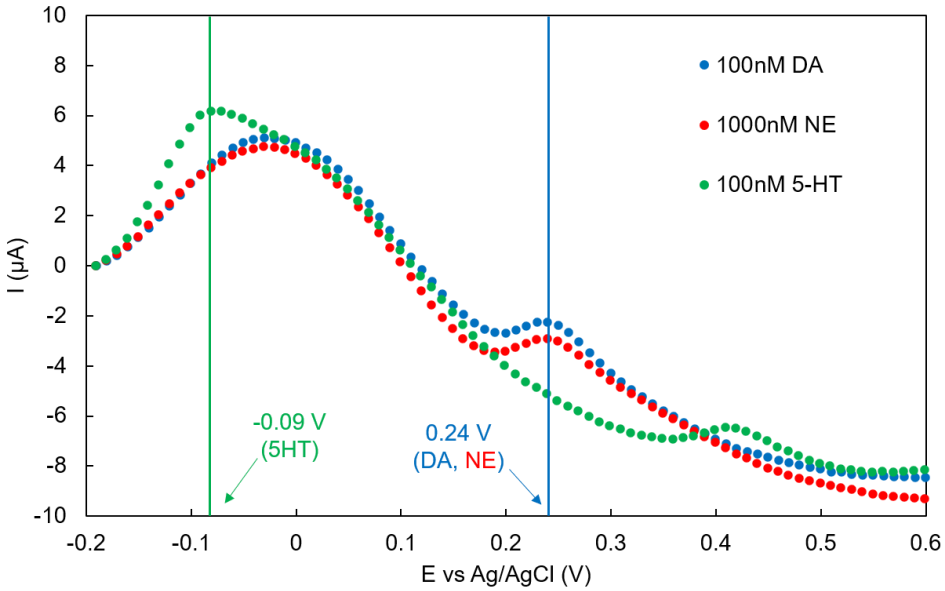

Figure S2 SWV voltammogram of DA (100 nM), NE (1000 nM) and 5-HT (100 nM) (thicker condition)

Oxidation potentials were observed at 0.24 V for DA and NE and at -0.09 V for 5-HT. These results suggest that both NE and 5-HT would be observed as the same peak because the oxidation potential of NE is the same as that of 5-HT. Subsequently, the SWV voltammograms of DA, NE, and 5-HT in the low concentration region of 0-100 nM are shown in **Figure S3(A)**, **(B)**, and **(C)**, respectively. **Figure S3 (D)** shows the calibration curves at 0.24 V for DA and NE and at -0.09 V for 5-HT. The slopes of curve in Fig. S3d are summarized in **Table S1**. Since no oxidation peak was detected in the voltammograms of NE and 5-HT up to 100 nM, calibration curves were prepared based on the oxidation potential at 1 μM at which the oxidation peak was detected.

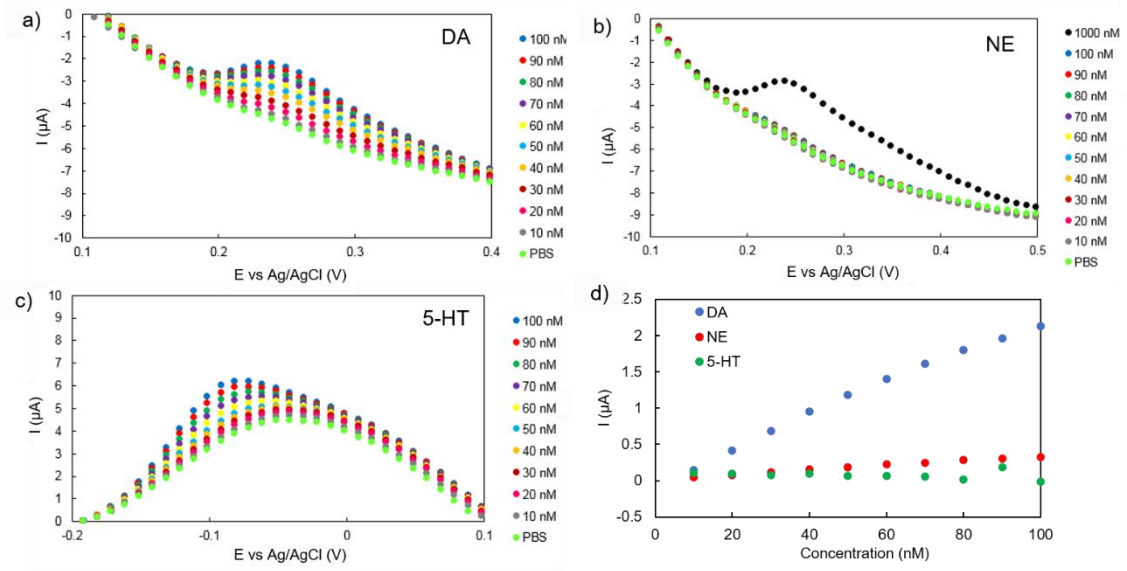

Figure S3 SWV voltammograms of a) DA, b) NE, c) 5-HT. d) Calibration curves of DA, NE and 5-HT measured with DA-PPy carbon electrodes

Table S1 Slope of the calibration curves of DA, NE and 5-HT

Transmitter	DA	NE	5-HT
Slope (nA/nM)	22±3.5	3.2±1.5	-0.6±1.9

In **Table S1**, the slope of the calibration curve of DA at 0.24 V was more than 6 times higher than that of NE and 5-HT. It is suggested that the sensitivity of DA at 0.24 V is sufficiently greater than that of NE or 5-HT, hence, DA can be selectively measured in the presence of NE or 5-HT.

4) Evaluation of the Surface Area of a DA-PPy Electrode on a Gold Electrode on a Polyimide Film (hereinafter referred to as a DA-PPy film electrode)

The quantification measurement of DA in DA solutions was carried out using a three-electrode cell with the DA-PPy film electrode with different areas (1, 0.5, 0.4, 0.3, 0.2, and 0.1 mm^2) as a working electrode. Each electrode was immersed in a well-degassed 0.1 mol/L phosphate buffer solution, and a 10 μM DA phosphate buffer solution was added to increase the concentration of DA by 10 nM to 100 nM, and square-wave voltammetry (SWV, scan range: -0.2 to 0.7 V, pulse height: 25 ms, pulse width: 25 ms, step height: 10 mV) was swept to measure the change in the oxidation current

of DA in the solution.

The SWV voltammograms of 0 - 50 nM solutions of DA were measured using DA-PPy film electrodes with electrode areas of 0.1 - 0.5 and 1.0 mm^2 as shown in **Figure S4**. The slope of the calibration curve for each electrode area is summarized in **Table S2**.

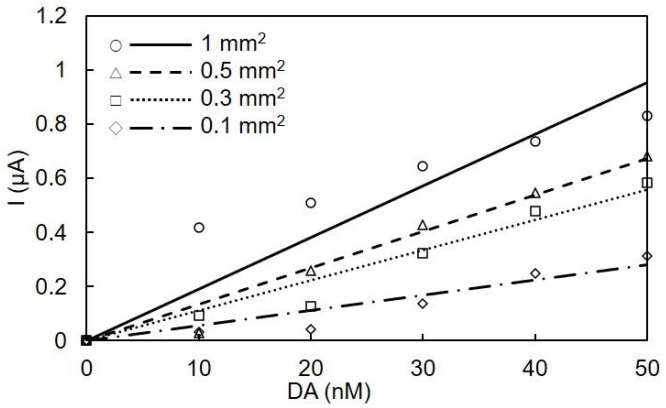

Figure S4 Calibration curves of DA obtained by using the DA-PPy film electrodes with different areas among 0.1, 0.3, 0.5 and 1.0 mm^2, respectively

Table S2 Slopes of the calibration curves of DA obtained by using film DA-PPy electrodes with different areas (n = 3)

Surface area (mm^2)	Slope (nA/nM)
1.0	21±10
0.5	19±4.4
0.4	12±12
0.3	13±15
0.2	5.7±5.1
0.1	7.2±4.7

From **Figure S4**, the current values increased in proportion to the DA concentration for electrode areas of 1.0 mm^2 and 0.5 mm^2, however, in the electrode area of 0.4 mm^2 or less, the slope

decreased and the concentration dependence deteriorated as the concentration increased. **Table S2** also showed that the initial slope was higher than 10 nA/nM for electrode areas of 1.0 mm^2 and 0.5 mm^2, while it was approximately 5 nA/nM for those of 0.4 mm^2 or less, with larger deviations among samples in comparison with those of larger electrodes. Based on the above results, we determined that 0.5 mm^2 is the smallest area where deviation is small and thus stable measurement is possible. In the following experiments in the text, DA-PPy film electrodes having the electrode area of 0.5 mm^2 were used.

5) Interference of ascorbic acid and uric acid on the DA-PPy film electrode

We conducted the same experiments in the presence of ascorbic acid (AA) and uric acid (UA) with changing their concentrations from 0 to 50 nM. As shown in **Figure S5**, there is no increase in current till 50 nM for both molecules, that clearly shows the specificity of the electrode to DA.

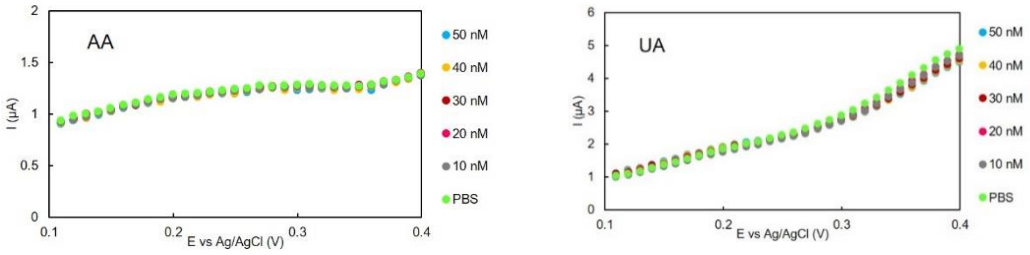

Figure S5 SWV voltammograms of AA and UA with DA-PPy film electrodes